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DILUTE SOLUTION REACTIONS OF THE NITRATE ION AS APPLIED TO WATER RECLAMATION

ADVANCED WASTE TREATMENT LABORATORY-I

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DILUTE SOLUTION REACTIONS OF THE NITRATE ION

AS

APPLIED TO WATER RECLAMATION

by

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for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

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Federal Water Pollution Control Administration
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FOREWORD

In its assigned function as the Nation's principal natural resources agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

Reports in this series will be distributed as supplies permit. Requests should be sent to the Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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ABSTRACT

A new and unexpected partial denitrification of dilute nitrate ion solutions (10 to 50 ppm NO_3^--N) has been achieved by treatment with 8 moles of ferrous sulfate per mole of nitrate in unbuffered alkaline reactions. The nitrogen loss, which probably represents evolution of N_2 or N_2O, has been as high as 50%. Total reduction to lost nitrogen plus nitrite and/or ammonia has approached 100%. The reduction takes place in the presence of partially oxidized black iron hydroxides, and requires catalytic quantities of cupric ion. Denitrification is suppressed by phosphates, as well as by several other factors, some as yet unidentified. Silver ion catalysis or a 16-fold excess of the ferrous salt permits reduction to ammonia in the presence of phosphate, but there is no accompanying denitrification.

Keywords: Nitrates, wastewater, denitrification, reduction, ferrous ion, catalysis, cupric ion

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INTRODUCTION

The presence of nitrate ion in water, reclaimed or otherwise, presents several distinct problems. In high concentrations, it can cause methemoglobinemia, a disease of the newborn, and it serves as a nutrient for algae at any concentration. Algae bloom becomes a problem in many aspects of water usage, such as the fouling of reclaimed waters in reservoir storage.

Although there have been numerous studies of methods of nitrate removal and control for use in water reclamation, removal by some direct chemical reaction, other than ion exchange, does not seem to have been given any really serious consideration in the past. This is not an oversight on the part of the interested scientific community; it is simply a reflection of circumstances that are not obviously amenable to attack by way of some common chemical reaction. For instance, if one considers a nitrate-N level of 10 ppm in water, then such ordinary reactions as quantitative precipitation or nitration of an organic compound cannot be brought to bear on removing nitrate from reclaimed waters. Precipitation requires expensive organic precipitants (e.g., "Nitron"), and nitration of organics is only accomplished in concentrated solutions.

Conversion of nitrate to a nitrogenous gas and denitrification by the evolution of such a gas is an attractive concept, and there are three gases that can be considered, although each has drawbacks (Ref. A1-A3). These are ammonia, nitrous oxide (N_2O) and nitrogen. (Such gases as NO_2, NF_3, NOCl, NO, and the like have to be discarded on the basis of reactivity, water solubility, or the simple impossibility of converting NO_3^- to such a gas in any simple reaction or series of reactions.) Ammonia has high water solubility, and requires a physical stripping step. It cannot simply be left in the water, since eventually, as part of the biological nitrogen cycle, it will be reconverted to nitrate. Nitrous oxide, while not nearly as soluble as NH_3, still has a fairly high water solubility compared to nitrogen. Nitrous oxide in solution does oxidize, albeit at a very low rate (Ref. A-1). Thus, at concentrations in the ppm range, N_2O could be subject to the same drawbacks as ammonia.

As far as chemical characteristics are concerned, nitrogen itself would be the ideal choice, since it has the lowest water solubility and greatest oxidation resistance of all the nitrogenous gases. However, in the oxynitrogen and hydronitrogen series of compounds, nitrogen is unique in that it is very difficult to obtain by simple reduction (Ref. A-3). While redox potentials often appear favorable, in the case of NO_3^- there is a large activation energy that must be overcome, and very strong reducing agents lead to NH_3 in most cases, while weaker ones take the nitrogen only to the +3 oxidation state.

Nitrogen evolution would be an attractive means of ridding water of nitrate ion, and the work described in this report was undertaken with

just that objective in mind, even though there appeared to be no simple one-step reaction sequence to go from NO_3^- to N_2. The premise of this work was that there might be efficient and economically attractive two-step reaction sequences that could be applied, based on reduction of nitrate to nitrite ion, and subsequent deammination of a primary amine with the nitrite. A model reaction series for this concept, using formaldehyde as the reducing agent and urea as the deammination agent is shown in equations (1) and (2).

$$2HNO_3 + HCHO \rightarrow 2HNO_2 + H_2O + CO_2 \quad (1)$$

$$2HNO_2 + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + 3H_2O \quad (2)$$

If applicable to dilute solutions of nitrate ion, these known reactions would be very attractive. The products N_2, CO_2, and H_2O are all innocuous, and based on bulk prices, a chemicals cost of 2 to 3 cents per thousand gallons could be projected for removal of NO_3^--N at the 10-20 ppm level.

Further consideration of the model reaction sequence allows one to speculate about other potential advantages of a direct chemical reaction. Incorporation of such a sequence into an existing plant might be possible by simply adding the appropriate metering devices to inject the reagents into the stream. A chemical process is easily adjusted to variable nitrate levels; there is no need to design for the maximum level, which would result in unused removal capacity during minimum flow periods. A chemical process can be turned on and off at will; the plant that experiences seasonal nitrification would be greatly benefited by having a process that it could start and stop on demand at the appropriate time of the year. Thus, flexibility and inherent reliability could make the reduction-deammination sequence more attractive than just simple economics might suggest.

While many reduction and deammination reactions are known and have been extensively studied, the conditions for such studies have been almost entirely restricted to relatively concentrated solutions. Dilute solution reaction chemistry of any type, let alone dilute solution reaction chemistry of specifically nitrate reduction and deammination, is an area of study which has been faintly touched at best. The objective of the present program was to select groups of candidate reduction and deammination agents that might possibly be used in water reclamatibn processes, and to test the feasibility of developing a denitrification process using these agents when the nitrate ion was present at dilutions of 10 to 50 ppm of NO_3^--N.

SUMMARY AND CONCLUSIONS

The objective of this program was to demonstrate the feasibility of denitrification by a chemical process. Although departing somewhat from the original reduction-deammination concept, such a demonstration was achieved in the course of the work.

After an extensive literature survey, eight reducing agents and three deammination agents were selected for testing the feasibility of denitrification by a reduction-deammination process. The original plan was to study various pairs of these agents in a statistically designed matrix of experiments, varying numerous environmental factors such as pH, temperature, etc. However, it soon became evident that unknown second-order interactions in the design could defeat the purposes of such a study. Accordingly, these eight reducing agents were screened under anaerobic conditions at high NO_3^--N concentrations (50 ppm) and high temperature (85° F) with the agent in excess, varying only pH and catalyst. On this basis, ferrous ion (Fe^{++}), iron powder, and hydrazine or its salts (N_2H_4, $N_2H_6SO_4$) showed appreciable reducing power. A very small amount of reduction was accomplished with glucose. Formaldehyde, carbon, sulfur dioxide, and carbon monoxide were inactive.

The deammination agents studied were sulfamic acid (HSO_3NH_2) and urea. Glycine was slated for study, but later abandoned. No nitrogen loss was detected that could be attributable to the deammination agents in any of the tests where reducing and deammination agents were studied together. Separate studies showed that urea was ineffective, and that sulfamate could only deamminate under acid conditions.

Of the three reducing agents that passed the screening, only ferrous ion was economically attractive; it is available as crude copperas, $FeSO_4 \cdot 7H_2O$, for only four dollars per ton. From the technical viewpoint, ferrous ion was the only choice, since the test series revealed that up to 55% denitrification was occurring with ferrous ion alone, apparently by direct reduction of NO_3^- to either N_2 or N_2O ("missing N").

Accordingly, the bulk of the experimental program was devoted to studies of the direct denitrification reaction with ferrous ion. Ferrous sulfate was used as the source of ferrous ion, but the solution must be initially basic, so that the system is actually heterogeneous, with precipitated ferrous hydroxide being the reducing agent. As the reaction progresses, the pH drops and the black ferrous-ferric complex is formed (Fe_3O_4 or the corresponding hydroxide). Assuming that the "missing N" evolves as N_2, then the reduction is a five-electron reaction, and since additional ferrous ion is consumed in forming the complex, the theoretical requirement for complete reduction would be 7.5 moles of Fe^{++} per mole of NO_3^-.

At the 10 ppm NO_3^--N level, using an 8:1 molar Fe^{++}:NO_3^- ratio, reduction (to mixtures of NO_2^-, NH_3, and "missing N") ranged from 50% to 100% and denitrification ranged from 10% to 45%. These results were obtained over an initial pH range of 7 to 11 using either lime or sodium hydroxide for pH adjustment. Neither reduction nor denitrification was observed under acid conditions. A trend for the amount of reduction to increase with increasing pH was noted, but the amount of denitrification did not seem to follow a trend.

Catalysis by either cupric ion (Cu^{++}) or silver ion (Ag^+) in 1-5 ppm concentration is necessary for reaction to occur, but denitrification was observed only when cupric ion was used as a catalyst. Addition of phosphate ion to the solutions interfered with catalysis by cupric ion, and no reduction occurred, even when the catalyst level was increased. However, at increased levels of iron (16:1 and 24:1), or with silver as the catalyst, reduction occurred readily. As before, no denitrification occurred when Ag^+ was the catalyst.

Carbonate ion did not interfere with the reduction reaction, but, again, no denitrification occurred when $CO_3^=$ was present. Carbonate buffered the solutions; this fact, coupled with other results where pH was held relatively constant by addition of base during the course of a run indicated that denitrification would not occur unless the pH was dropping as the reactions progressed - that is, buffering prevented denitrification.

Based on these results, development of a denitrification process based on direct chemical reduction of nitrate ion to nitrogen or N_2O appears feasible. The denitrification can be carried out with an inexpensive reducing agent (copperas) and is worthy of further technical evaluation. However, much more will have to be known about the basic chemistry of this reaction before a definitive process emerges.

The effect of pH and buffering on the reaction needs to be resolved since there is no evident explanation for the absence of denitrification under constant pH conditions. Quite possibly, observation of denitrification has been obscured by the effect of some unknown variable. The fact that the amount of denitrification does not correlate with pH level, and that there has been an occasional failure to denitrify even in the absence of buffering, indicates that such a variable may indeed exist. The heterogeneity of the system could be the source of this inexplicable behavior. Minor variations in the mode of precipitation of the ferrous hydroxide, the manner of absorption of catalyst ions and the degree to which this precipitate absorbs them, the manner in which the ferrous-ferric complex forms, and a number of other factors relative to the solid phase could all play a role, and consistent denitrification and reduction might well prove to be a function of consistent precipitation technique.

Of great importance, too, is a determination of the identity of "missing N", and an investigation of the intermediates that lead from NO_3^- to "missing N". Obtaining total denitrification may well depend on steps in the mechanism that are not evident in the present work. For instance, if N_2 is the gas evolved, the denitrification could actually be the result of the oxidation of N_2H_4 or NH_2OH formed at some intermediate stage. The possibility of loss of nitrogen in some form as a part of the precipitated iron insolubles should also be investigated, even though such a mode of denitrification seems unlikely.

Further studies are also required on catalysis of the reaction. Cupric and silver ions are the classical catalysts for homogeneous reductions, yet ferrous ion reduction/denitrification reaction is apparently heterogeneous. Cupric and silver ions are definitely different in their response to phosphate, and apparently different in their ability to lead to denitrification, although this last difference could again be confounded with some other variable.

With the information now at hand, there are three possible approaches to development of a ferrous ion denitrification process as described below.

The first approach, total denitrification with ferrous ion, assumes that further studies of the reaction will result in the data necessary to make reduction of NO_3^- to "missing N" by ferrous ion both consistent and close to quantitative.

In the second approach, a reduction-deammination sequence, reduction and some denitrification is carried out by the ferrous ion, and the pH falls from some initially alkaline value to below 7 as the reaction progresses. If NO_2^- were the major reduction product other than N_2O or N_2, then deammination might still be used to complete the denitrification. However, carbonate ion would have to be absent for this sequence to take place, which would severely limit the applicability of this process.

The third possible process, coupling ferrous ion reduction with ammonia stripping, might be the easiest to develop. In some of the reactions conducted during this study, 33-45% denitrification occurred, and another 34-46% of the nitrate was converted to ammonia. Thus, a sequential ferrous reduction-ammonia stripping process has demonstrated potential of up to 90% total denitrification.

LITERATURE SURVEY

Approximately one-third of the effort on this program was devoted to a comprehensive literature search, covering the period from early 1968 well back into the nineteenth century. Recent references were obtained from Keywords (Chemical Abstracts), Chemical Titles, Current Contents, Water Pollution Abstracts, and on-the-shelf journals and reports. For the period back through 1907, Chemical Abstracts and the annual literature reviews in the Journal Water Pollution Control Federation were prime sources. Gmelins Handbuch der anorganischen Chemie revealed references back to the early 1800's. A patent search was conducted by the North American Rockwell Patent Department, and several pertinent current references were provided by the FWPCA Project Officer, Dr. R. B. Dean.

While the primary objective of the search was selection of suitable reduction and deammination agents for subsequent laboratory testing, much related information was collected on water reclamation in general, and nitrified waters in particular. Between 400 and 500 references were collected in original or abstracted form.

For this report, slightly more than 200 references to the most pertinent and informative articles are provided.

The "Discussion and Results" section, which follows, contains references to the literature sources which, for the convenience of the reader, are grouped as follows in the section entitled "References":

A. Nitrates in Water

1-4	General Chemistry
5-30	Occurrence and Effects
31-48	Natural and Biological Denitrification
49-68	Elimination Methods

B. Water Reclamation

1-12	Conventional and Tertiary Treatment
13-25	Iron Salts in Water Treatment
26-30	Carbon in Water Treatment

C. Reducing Agents for Nitrate

1-23	Ferrous Salts
24-28	Carbon
29-33	Sulfur Dioxide
35-47	Formaldehyde
48-56	Sugars
57-61	Powdered Iron
62-69	Hydrazine and its Salts
70-85	Miscellaneous

D. Deammination Agents

1-14	Sulfamic Acid
15-21	Urea
22-24	Amino Acids
25-34	Miscellaneous

E. Catalysis

1-6 (Not subdivided)

F. Analytical Methods

1-9 (Not subdivided)

DISCUSSION AND RESULTS

BACKGROUND

Nitrates in Water-Occurrence and Effects (See References A-5 through A-30)

Nitrates occur in natural and reclaimed waters in amounts ranging from a fraction of a part per million to several hundred ppm, calculated as nitrate-nitrogen (NO_3^--N). The sources may be natural, such as leaching from nitrate deposits (e.g., guano in limestone cave areas), the natural decay and oxidation of nitrogenous organic matter (protein) as carried out by certain microorganisms, and the fixation of atmospheric nitrogen as NO and NO_2 from electrical discharges during thunderstorms. The sources may also be man-made, such as leaching from agricultural lands treated with nitrogenous fertilizers, effluent from fertilizer manufacturing plants, and effluent from other chemical and manufacturing processes that employ nitrates in one form or another.

In water reclamation, nitrate ion may find its way into the stream initially from any of the above sources. However, regardless of the initial water quality, secondary treatments based on biological oxidation of organic matter (i.e., activated sludge and trickling filter processes) can themselves introduce additional nitrate. Hence, almost all secondary effluent contains an appreciable quantity of nitrate ion.

There are two distinct problems associated with nitrates in water: methemoglobinemia and algae bloom. Methemoglobinemia is a serious and often fatal disease of the new-born, characterized by cyanosis, for which nitrates have been designated a causative factor. A drinking water standard of 10 ppm NO_3^--N has been established by the Public Health Service (Ref. A-30) as a preventive measure for this disease.

Both ammonium and nitrate ions, as well as phosphates, are excellent nutrients for plants, including algae (Ref. A-14). Algae bloom is one aspect of a natural process called eutrophication, wherein a body of water such as a lake is gradually converted into a swamp and eventually a meadow. The beginning and end of this process are not particularly unpleasant; however, in the intermediate stages, algae and aquatic plants grow in abundance as nutrients build up, this abundant organic matter decays depleting oxygen and killing the aquatic fauna. Unfortunately, man-made sources of nutrients accelerate this process, and induce the algae bloom stage in receiving waters where it would not otherwise occur. Eutrophication would be intolerable in a reservoir to be used for reclaimed water for drinking purposes. Other water uses, such as recreation, incorporate a certain esthetic value which is certainly not enhanced by overgrowths of algae.

Natural Denitrification (See References A-31 through A-46)

Countering the natural and man-made nitrification processes are natural denitrification processes. The conditions for nitrification and denitrification are very similar, with the main difference being that denitrification occurs only when the water is close to being depleted of oxygen. Under such conditions, certain microorganisms will continue the oxidative degradation of organic matter, using the nitrate ion as the oxygen source, and eliminating the nitrogen as N_2 gas. Denitrification can occur in water, in soils, and in accumulated masses of organic matter such as silage (Ref. A-37, A-44). Good reviews of natural denitrification processes are presented by the Thames Survey Committee (Ref. A-47) and by Camp (Ref. A-34). The latter author, however, implies that natural denitrification can be partly chemical, and uses the deammination reaction of nitrite ion with urea as an example, showing the reaction to be thermodynamically favorable. Chemical reduction by ferrous salts is also believed to play a role in natural denitrification in certain soils (Ref. A-31, C-22) and acid tropical waters (Ref. A-46). However, it is generally agreed that most natural denitrification is biological rather than chemical (Ref. A-33).

In the water reclamation field, natural denitrification first came to attention as a problem (Ref. A-32, A-38 through A-42). The nitrogen evolved, when natural denitrification occurs in sedimentation basins, causes the phenomenon known as "rising sludge" or "rising humus". That is, bubbles of nitrogen entrapped in the sludge carry it to the surface rather than allowing it to settle. In recent times, natural denitrification has been turned to good use, and forms the basis for several advanced waste treatment processes (Ref. A-36, A-43, A-46, A-55). These processes are reviewed below.

Nitrate Removal Processes (See References A-49 through A-68)

There have been a number of methods studied for producing denitrified water. These include: control of secondary treatment processes in such a manner that nitrification is minimized; ion exchange; extraction; and biological denitrification. Adsorption of nitrate on such substrates as carbon, alumina, and silica gel has also been noted, but does not seem to have been studied for the specific purpose of developing a removal process. An occasional excursion into reaction chemistry has been made (Ref. C-23, C-58) using ferrous salts and iron powder, but with little or no success. However, concentrates (primarily radioactive wastes) have been successfully treated with formaldehyde and sugars as reducing agents, as discussed later in this section.

Controlling the secondary treatment processes can be effective, but suppression of nitrification is often accompanied by some undesirable effect, such as decreased BOD removal. (BOD, Biochemical Oxygen Demand, a measure of the biodegradable organic content of the water.) Ion exchange is very efficient, but costs can be high. Extraction works very nicely on

concentrates, but is inefficient for dilute nitrate solutions. Apparently, none of these processes are under serious consideration at the present time for extensive incorporation into reclamation plants. A more detailed picture of the state-of-the-art of these processes, as well as processes designed to remove ammonia, may be found in the recent publication of Farrell, Stern and Dean (Ref. A-55).

Biological denitrification is currently under active study (Ref. A-46). There are two modifications of this process. The first (Ref. A-36) involves a sequence which first nitrifies the water to the greatest extent possible, then carries the water into an anaerobic chamber where sludge from a previous step is used to supply organic food to the denitrifying microorganisms. The second modification has grown from the unexpected denitrification observed when activated carbon columns were being studied for tertiary treatment (Ref. A-43). In this case, the denitrifying organisms had established themselves in the carbon columns. Supplying methanol as additional food for the bacteria increases the efficiency of this process, and sand has been successfully substituted for the carbon.

SURVEY OF CANDIDATE REDUCING AND DEAMMINATION AGENTS

Chemicals in Water Reclamation (See References B-1 through B-30)

In choosing agents for the reduction-deammination study, attempts were made, wherever possible, to project the tentative process in terms of other current and future processes to see where the new process might be conveniently incorporated.

In general, it appears that flocculation and coagulation will play an increasing role in the future, using either lime or alum. (See Ref. B-1 for a tabulation of well-developed tertiary treatments.) Lime flocculation can reduce phosphate ion concentration, so it is reasonable to expect the waters to be highly basic during some stage of reclamation processes aimed at controlling nutrient content. The lime is often used with another salt as an additional coagulant. Ferrous and ferric salts (Ref. B-13 through B-25) have been used in this manner. Finally, activated carbon may be used in the final stages to remove the last traces of organic matter (Ref. B-26 through B-30). Both ferrous salts and carbon are potentially reducing agents for NO_3^- ion, and are discussed further below.

Choice of Reducing Agents

Eight reducing agents were selected for study as a result of the literature survey. The information amassed on each of these is summarized below.

Ferrous Ion (Ref. C-1 through C-23). Ferrous ion, as either ferrous sulfate or ferrous hydroxide, has formed the basis for many analytical determination of nitrate ion, converting the NO_3^- to NH_3. The first step, conversion to nitrite ion (NO_2^-), is slow but may be catalyzed by silver or cupric ions. Subsequent reductions proceed to ammonia by attacking NO_2 and NO from the $HNO_2/NO_2/NO/H_2O$ equilibrium. A summary of almost all possible reaction sequences is given in Ref. C-22. The reduction is most effective under faintly or strongly basic solutions, but can also occur under acid conditions. It has been stated that the concentration of ferrous ion must be at least 70 ppm in order to be effective (Ref. C-4).

Ferrous ion was once studied for use in water reclamation, and was shown to be capable of 90% conversion of NO_3^- to NH_3 at the 100 ppm NO_3^--N level (Ref. C-23). This work was abandoned because of the "ferrous and ferric hydroxide sludges" that formed. From an operational viewpoint, this is difficult to understand, because the "sludges" are heavy, settle easily, and so should be easy to separate from the treated water. However, ultimate disposal of the "sludges" may pose some problems (Ref. B-13), and will have to be given serious consideration in the development of any process based on ferrous ion.

As noted earlier, some of the natural denitrification and reduction in water and soils has been attributed to the presence of ferrous salts (See page 9).

Carbon (Ref. C-24 through C-28). Nitrate can be reduced to nitrite by carbon, with CO_2 being the other product. The well-known "wet-ashing" technique for removal of carbonaceous materials in analytical procedures is a good example. Coal, carbon black, and graphite reduce nitrate. However, high concentration and heating are generally required, under which conditions mixtures of nitrogen oxides are evolved.

Sulfur Dioxide (References C-29 through C-33). Sulfur dioxide, if shown to be suitable as a reducing agent, could play a dual role in water reclamation because of its bacteriostatic properties. Sulfur dioxide can reduce nitrate to various products, including hydroxylamine (Ref. C-33). The most pertinent article (Ref. C-31) claimed that a 10% NH_3 solution saturated with SO_2 until faintly ammoniacal would reduce oxidizing anions and completely eliminate nitrite ion as N_2.

Formaldehyde (References C-35 through C-47). Formaldehyde has been extensively studied as a reducing agent for nitrate concentrates ("Purex wastes") by the Atomic Energy Commission. Under these conditions, NO and NO_2 are evolved, which implies that HNO_2 would be the product in dilute aqueous solution. There is an induction period in the reaction which can be overcome by ferric ion catalysis (Ref. C-42, C-43).

One of the few articles dealing with dilute solution reduction of nitrate ion has some interesting information on formaldehyde (Ref. C-36). In the photochemical reduction of nitrate to nitrite, with the results expressed as a ratio $(R = \frac{NO_2^-}{NO_3^-})$, it is shown that the R value is increased by a factor of 3 to 4 by the addition of formaldehyde. Working with a 0.05% KNO_3 solution, the value for R was 60 after 20 minutes of ultraviolet radiation in the presence of formaldehyde, representing a change in NO_3^--N concentration of about 70 ppm down to 1 to 2 ppm. The data did not explicitly show, however, that part of the reduction was by direct reaction with formaldehyde rather than being totally photochemical in nature.

Sugars (References C-48 through C-56). Sugars have also been used by the Atomic Energy Commission to reduce nitrate concentrates. Sugars also increase the R value in the photochemical reduction of NO_3^- (see above). A sugar need not be one of the classical reducing sugars to react readily with nitrate: sucrose as well as glucose is suitable.

Powdered Iron (References C-57 through C-61). Powdered iron is similar to ferrous ion in the manner in which it reduces nitrate. It was once examined as a reducing agent for eliminating nitrate ion from drinking water, but was classed as ineffective because it did not convert NO_3^- directly to N_2 (Ref. C-58). The efficacy of powdered iron as a reducing agent depends to some extent on its method of manufacture (Ref. C-59).

Hydrazine and its Salts (References C-62 through C-69). Hydrazine is an excellent reducing agent for nitrates, and forms the basis for the Auto Analyzer now used for analysis of various waters (Ref. C-63, C-67). The reader should note that this reduction reaction, if it is to be of value in the proposed process, must lead to near-quantitative oxidation of the hydrazine to N_2. If this does not occur, then the reaction may introduce more inorganic nitrogen compounds into the water than are removed by the overall process.

Carbon Monoxide. Carbon monoxide was selected as an agent purely on the basis of economy and the desirability of having CO_2 as a byproduct. No references to CO/NO_3^- reactions were found; on the contrary, a very early reference (1851) clearly states that carbon monoxide and nitric acid do not react (Ref. C-83).

Miscellaneous Reducing Agents (References C-70 through C-85). Other reducing agents noted during the course of the literature survey were generally metals and various lower-valent salts of metals (e.g., Al, Ti^{++}, Cu-Cd, Sn^{++}, etc.). These were eliminated from consideration on the basis of undesirable byproducts and/or expense.

Choice of Deammination Agents

Three deammination agents were selected, based on the information presented below.

Sulfamic Acid (References D-1 through D-14). Based on an article comparing sulfamic acid and urea (Ref. D-14), sulfamic acid was the prime choice for deammination. This article showed quantitative reaction of the theoretical amount of sulfamic acid and nitrite ion in two minutes even at the 2 ppm NO_2^--N level, whereas even excess urea could not effect complete deammination at that nitrite concentration after one hour. The system sulfamic acid-nitrite ion has been studied extensively in analytical applications, in terms of the intermediates formed, and with respect to thermodynamics. A means for removing nitrite ion from boiler water using sodium sulfamate has been patented (Ref. D-13).

It should be noted that sulfamic acid can react with nitrate ion as well as nitrite, yielding N_2O. However, this reaction is very slow below 60° C (Ref. C-7).

Urea (References D-15 through D-21). As noted above, urea is not nearly as effective as sulfamic acid for deammination, although its use has been patented for treating waters to remove nitrite ion (Ref. D-15, D-21).

Amino Acids (References D-22 through D-24). Since amino acids are present in water during various stages of reclamation processes, they might provide an *in situ* source of deammination agent. Glycine was chosen as the model originally, since it reacts readily with nitrate, although side reactions give some CO_2 and N_2O as well as nitrogen (Ref. D-22). Comparative studies (Ref. D-23) have shown that relative to alanine (1.00), most amino acids, glycine included, are deamminated at about the same rate (0.70 to 1.50), although there are extremes such as cystine (3.12) and isovaline (0.14).

Miscellaneous Deammination Agents (References D-25 through D-34). In general, all primary organic amines and amides are susceptible to deammination by NO_2^-. Azides also react with nitrite in a similar fashion. However, none of these offer any particular advantage over the agents discussed earlier, and, of course, the organic amines will leave an organic residue, which is not desirable.

Ammonia and its salts generally require heating in order to react with nitrites at appreciable rates. However, it was tentatively planned to test ammonia in combination with SO_2, in view of the data presented earlier (p. 11) on this particular combination.

Catalysis in Reduction and Deammination (See References E-1 through E-6)

Catalysis plays a role in many of the reactions mentioned earlier, i.e., iron and ferrous ion reductions are catalyzed by cupric or silver ions, hydrazine reductions by cupric ion, formaldehyde reductions by ferric ion. Catalysis has a role in certain biological nitrate reductions as well (Ref. E-3).

Cupric ion and silver ion are the classic homogeneous reduction catalysts, particularly for homogeneous reductions with hydrogen (Ref. E-4). Of interest to the present program is the fact that catalytic activity of these ions may be enhanced more than a hundredfold in the presence of organic acids. Magnesium, cadmium, and zinc ions are also reported to be active catalysts in the presence of organic acids.

An article published in 1923 (Ref. E-5) reports that nitrate ion reduction is an autocatalytic process, and that in the absence of some small initial concentration of nitrite ion, nitrate cannot be reduced by ferrous ion, formaldehyde, mercurous ion, or a number of other agents. Nitrite ion was removed from the test solutions with urea and amino acids. If this phenomena were indeed confirmed, it would mean that reduction and deammination would have to be sequential operations. However, the conclusion is refuted to some extent by other work; the simultaneous reduction-deammination cited earlier for NH_3/SO_2 solutions is one example.

DILUTE SOLUTION REACTION STUDIES

Screening of Reducing Agents

The initial laboratory plan in this program called for a series of statistical test matrices, studying reducing-deammination pairs, with high and low levels of the variables as given in Table 1.

Each test solution was to be sampled after reaction times of one hour and 24 hours. Each sample was to be analyzed for nitrate, and if reduction had occurred, for nitrite and ammonia to determine the total nitrogen balance.

In selecting the levels of variables, it was assumed that the denitrification treatment would be applied to secondary effluent, and the values for pH and temperature are believed to be the extremes. A different pH range was chosen for ferrous ion, Fe^{++}, since in this case it was assumed that ferrous treatment would be coupled with lime coagulation, and the denitrification would thus be carried out in alkaline waters.

The initial tests within the first matrix, if accepted at face value, would have led to the strange conclusion that ferrous ion could not even

TABLE 1

REDUCTION-DEAMMINATION REACTION VARIABLES

Variable	High Level	Low Level
NO_3^--N Concentration	50 ppm	10 ppm
Temperature	85° F	45° F
pH (Fe^{++} excepted) (with Fe^{++})	9 11	6 8
Reducing Agent Concentration	Threefold excess	Stoichiometric
Deammination Agent Concentration	Threefold excess	Stoichiometric
Order of Addition	Deammination agent added one hr after reducing agent	Agents added simultaneously
Atmosphere	Nitrogen (water deaerated)	Air (water untreated)
Catalyst	1 to 5 ppm of Cu^{++} or Fe^{+++}	No catalyst

reduce nitrate ion, let alone participate in a denitrification sequence. In view of the large amount of literature that had been uncovered on the reducing power of ferrous salts, this result appeared to be anomalous.

In statistical terms, the apparent anomaly arose because the results were confounded by a second-order interaction of variables. The matrix design was such that air oxidation of ferrous ion was predominant in catalyzed tests, and the rate of the uncatalyzed reactions was essentially nil at the low concentration levels.

Since much less information was available on the other seven reducing agents, it was decided that statistically designed matrices with a large number of variables could not be conducted with any degree of assurance that other unrecognized interactions would not lead to fallacious conclusions. Accordingly, a new test series was devised to screen the reducing agents with most of the variables fixed at the high levels.

Only the effects of pH, catalyst, and deammination were studied in this new series, with the deammination agent added either initially after 24 hours, or not at all. However, the deammination agents had no effect on these reactions, as discussed later in this section. The results of the new tests, which amounted to screening the candidate agents for reducing power under the most favorable conditions possible, are given in Table 2.

On the basis of these tests, only ferrous ion (Fe^{++}) appears to be a potentially useful agent. Hydrazine and its salts, since they did not achieve quantitative reduction, introduced more inorganic nitrogen than they could remove. Iron powder is considerably more expensive than Fe^{++} ion. The latter is available as crude copperas, at a cost of a few dollars (less than $5.00) per ton, while the most optimistic estimates for iron powder are in the area of 10 cents per pound.

Deammination Agents

Deammination agents (urea, or sulfamic acid initially neutralized to avoid additional pH adjustments) were present in many of the tests cited above, but once Fe^{++} ion had emerged as the prime reducing candidate, the deammination phase of this effort was stopped. The Fe^{++} reduction must be carried out under initially basic conditions, and sulfamate deamminates effectively only under strongly acid conditions. This conclusion was reached during a separate series of studies carried out as part of the supporting analytical effort (See p.35). The poor performance of urea, as cited in the literature (Ref. D-14), was also confirmed. At the 3 ppm NO_2^--N level, no deammination could be detected after 48 hours at either pH 4.0 or 10.6, even though the urea was present in threefold excess.

Glycine was slated to be studied as a deammination agent, but was bypassed as the investigation of ferrous ion proceeded.

TABLE 2

REDUCING AGENT SCREENING

Reducing Agent	Conditions Varied (and number of tests)	Reduction Observed, %
SO_2	Fe^{+++}, Cu^{++} catalysts; pH 6 and 9 (4 tests)	None
Carbon	Fe^{+++}, Cu^{++} catalysts; pH 6 (4 tests)	None
CH_2O	Fe^{+++}, Cu^{++} catalysts; pH 6 (4 tests)	None
CO	Cu^{++} catalyst; pH 6 (2 tests)	None
Glucose	Fe^{+++}, Cu^{++}, V^{+5} catalysts; pH 4 and 6 (6 tests)	3 to 6 (with V^{+5} only)
N_2H_4	Fe^{+++}, Cu^{++} catalysts; pH 11 (4 tests)	10 to 40 (none with Fe^{+++})
$N_2H_6SO_4$	Cu^{++} catalyst, pH 11 (4 tests)	10-20
Fe Powder	Cu^{++} catalyst, pH 6 (3 tests)	15-45
Fe^{++} Ion	*Cu^{++} catalyst, pH 11 (6 tests)	15-40

Fixed Conditions:

Temperature:	85° F
Test Time:	48 hr.
Atmosphere:	Nitrogen
NO_3^--N Concentration	50 ppm
Reducing Agent Concentration:	3X (Denotes 3 moles of reducing agent for each mole of NO_3^-)

* Tests with Fe^{++} slightly more complex. Discussed in more detail in the text.

FERROUS ION AS A DENITRIFICATION AGENT

Initial Screening Studies

As noted in Table 2, the initial screening tests with ferrous ion were slightly more complex than those with the other reducing agents. The initial matrix tests had indicated that bubbling air through the solutions oxidized the Fe^{++} before it could reduce NO_3^- in cases where catalyst was present, and that uncatalyzed reactions were not possible at high dilutions. However, there was still the possibility that there was an interference from the deammination agent, either direct or by suppression of the autocatalytic influence of NO_2^- ions, as had been indicated in the literature (Ref. E-5. See p. 14 for discussion). Accordingly, the first screening tests with Fe^{++} incorporated the sulfamate addition time and presence or absence of NO_2^- ion as variables. Test conditions and results are given in Table 3.

The above data indicate that nitrite does not catalyze the reduction, and that sulfamate does not interfere with the reduction. If anything, sulfamate aids reduction; more reduction occurred in Tests 3 and 4 where sulfamate was added initially. Of course, under the basic conditions, sulfamate did not deamminate; decreases in nitrite ion occurred only as the NO_2^- was oxidized back to nitrate. This was quite evident in the blank and in some of the other tests. Oxidation occurred because of traces of oxygen in the house nitrogen used to blanket the reactions, or possibly because air was introduced when the 24 hour samples were taken.

The really significant result, however, is the total nitrogen balance that resulted at the end of Test 3. Of 49 ppm of nitrogen initially present, only 39.2 ppm could be accounted for after 48 hours. These data lead to the conclusion that Fe^{++} can reduce nitrate ion directly to either N_2 or N_2O, which can escape from the reactor. Since the actual constitution of the escaping material has yet to be determined, it is generally referred to in this report as "missing N".

The precipitated iron insolubles in these reactions were black, which indicated that the iron end product was not ferric hydroxide, but the mixed $Fe^{++} \cdot 2Fe^{+++}$ salt; that is, Fe_3O_4, or the corresponding mixed hydroxide, although the existence of the latter does not seem to have to be definitely established. Thus, a balanced equation for the reduction of nitrate to nitrite should be written as in Equation (3).

$$H_2O + 3Fe^{++} + NO_3^- \rightarrow Fe^{++} \cdot 2Fe^{+++} + NO_2^- + 2(OH^-) \qquad (3)$$

The denitrification reactions may be as those shown by Equations (4) and (5).

$$12Fe^{++} + 2NO_3^- + 5H_2O \rightarrow 4(Fe^{++} \cdot 2Fe^{+++}) + N_2O + 10(OH^-) \qquad (4)$$

$$15Fe^{++} + 2NO_3^- + 6H_2O \rightarrow 5(Fe^{++} \cdot 2Fe^{+++}) + N_2 + 12(OH^-) \qquad (5)$$

TABLE 3

FERROUS ION REDUCTION OF NO_3^-

Test No.	Conditions Varied	Time, hr.	Analytical Results, ppm		
			NO_3^--N	NO_2^--N	NH_3
1	Sulfamate added after 24 hrs. No NO_2^-.	0	48.3	--	--
		24	38.5	--	--
		48	38.9	--	--
2	Sulfamate added after 24 hrs. NO_2^- added.	0	49.6	5.0	--
		24	43.4	--	--
		48	43.9		
3	Sulfamate added initially. No NO_2^-.	0	49.0	--	--
		24	30.2	6.7	--
		48	33.0	4.4	1.8
4	Sulfamate added initially. NO_2^- added.	0	48.5	--	--
		24	28.5	9.7	--
		48	34.5	4.3	--
5	Blank (No Fe^{++}). NO_2^- added.	0	50.0	4.2	--
		24	50.9	3.9	--
		48	54.7	0.8	--

Fixed Conditions:

Temperature:	85° F
Atmosphere:	Nitrogen
pH:	11
NO_3^--N Concentration:	50 ppm
Fe^{++} Concentration:	3X } (Denotes 3 moles of agent per mole of NO_3^-)
Sulfamate Concentration:	3X)
Catalyst:	Cu^{++}, 5 ppm

Finally, some of the nitrate is reduced to NH_3, as in Equation (6).

$$12Fe^{++} + NO_3^- + 6H_2O \rightarrow 4(Fe^{++} \cdot 2Fe^{+++}) + NH_3 + 9\ (OH^-) \qquad (6)$$

These latter reactions (Eq. 4, 5, 6) have a much greater iron demand than the simple 2 electron NO_3^-/NO_2^- reduction. In fact, if it is assumed that the "missing N" in Test 3 evolved as N_2, then the reduced products (NO_2^-, N_2, and NH_3) account for about 80% of the ferrous ion that was originally present. That is, reduction of NO_3^- by Fe^{++} is a fairly efficient process, but in this first screening series there simply was not enough of Fe^{++} to reduce all the NO_3^- via the 4, 5, and 8 electron reactions shown.

Denitrification was confirmed in additional screening tests, carried out with the Fe^{++} ion concentration increased to eight times that of the NO_3^- ion on a molar basis (designated as "8X" concentration). This would be slightly more than enough ferrous ion to convert all the NO_3^- to N_2, assuming N_2 to be the denitrification product. In this series, pH and catalyst level were varied. No deammination agent was present in this or any subsequent studies.

The data in Table 4 clearly show that as much as 50-55% denitrification can occur as a result of direct Fe^{++} reduction of NO_3^-. The data also show that denitrification does not occur under initially acid conditions. The effects of catalyst level and pH are not clearly separated, however, and no ready explanation can be given for the reversal of the NO_3^--N and NO_2^--N levels shown in the "duplicate" 3a and 3b tests.

Attempted Identification of "Missing N"

Following the above screening tests, an attempt was made to identify the "missing N" by carrying out the reaction in a closed, evacuated vessel, using carefully degassed solutions, and examining the evolved gases mass spectrometrically. This experiment failed because no denitrification occurred, for reasons unknown. The conditions (except for the atmosphere) were the same as those shown for tests 3a and 3b in Table 4. However, the mass spectrometer detected only trace amounts of nitrogen and argon (residual air) after trapping out the water vapor, and analyses of the solution showed NO_3^--N, 1.1 ppm; NO_2^--N, 21.3 ppm; and NH_3-N, 25.8 ppm. (48.2 ppm total for a nominal 50 ppm NO_3^--N initial concentration.)

Identification of "missing N" was planned for some later stage, once the reaction was more fully understood. However, other aspects of the reaction took on a greater priority, and these plans were never carried out. Nonetheless, these results are of importance: they show that occasionally, for reasons as yet unknown, the denitrification reaction fails completely. Accordingly, results discussed subsequently in this report must be interpreted with caution since the occasional failure from unknown causes can be a confounding factor.

TABLE 4

DENITRIFICATION WITH FERROUS ION

(Duplicate Tests)

Test No.	pH	Cu^{++} ppm	Time, hr.	Nitrogen Balance, ppm			
				NO_3^--N	NO_2^--N	NH_3-N	"Missing N"
1. a	4.0	5	0	50	--	--	--
			48	50	--	--	--
b	4.0	5	0	50	--	--	--
			48	50	--	--	--
2. a	7.1	10	0	50	--	--	--
			24	25.8	--	--	--
			48	6.8	0.5	16.5	26.2
b	7.1	10	0	50	--	--	--
			24	35.2	--	--	--
			48	6.1	0	19	24.9
3. a	11.0	5	0	50	--	--	--
			24	3.0	16.0	19.5	11.5
			48	2.6	14.6	--	--
b	11.0	5	0	50	--	--	--
			24	15.3	4.3	19.1	11.3
			48	13.3	4.3	--	--

Fixed Conditions:

Temperature:	85° F
Atmosphere:	Nitrogen
NO_3^--N Concentration:	50 ppm
Fe^{++} Concentration:	8X

As a final check, the possibility of "missing N" being removed from the system along with the precipitated iron insolubles should be tested, even though this mode of denitrification seems very unlikely. There are no known insoluble nitrates or nitrites that can form in this system, and while metal oxides and their gels (e.g., alumina, Ref. A-50, A-60) have been shown to absorb NO_2^- and NO_3^- ions, such absorption is extremely inefficient, even in concentrates.

The catalyst ions are also undoubtedly incorporated, at least in part, into the insolubles. However, loss of nitrogen as a cupric ammine, such as $Cu(NH_3)_4^{++}$, is also unlikely. For instance, in tests number 2a and 2b (Table 4) the molar ratio of "missing N" to cupric ion approaches 12 to 1. Thus, much more denitrification occurs than can be accounted for by the formation of a cupric ammine.

Also, as will be discussed subsequently, the pH drops as the reaction progresses. With an initial pH near 7 (as in tests 2a and 2b), the final pH will be near 5. The simple ammine complexes dissociate readily under acid conditions.

There are a few known complexes of N_2O with salts, such as $K_2SO_4 \cdot N_2O$ (Ref. A-4). These behave much like the ammines; the N_2O is liberated from such species in dilute acids. Thus, although complexes of ammonia or N_2O might well play a role in the mechanism of the reaction during its initial alkaline stage, it does not appear that any significant part of the denitrification can be attributed to complex formation and loss of such complexes as part of the insoluble materials.

Effect of pH on Denitrification

All results reported in this section and the remainder of this report were obtained at a 10 ppm NO_3^--N concentration, in order to generate data at a level near that of the average secondary effluent. The effect of varying pH is shown in Table 5.

There is no readily evident correlation of pH and denitrification from these data, even excluding the apparently anomalous results in Test 5a. There is a discernible trend for increased reduction with increased pH, particularly if one considers the extremes (4.3 ppm average residual NO_3^--N at pH 7.0, 0.2 average residual at pH 11.0).

With the exception of Test 7, the predominant reduced products were "missing N" and ammonia. In tests 3 and 6, these two products accounted for 70 to 90% of the total nitrogen. A combination of processes, where ferrous ion denitrification would be followed by ammonia stripping, thus has the potential for close to complete denitrification.

It should be noted that pH was not constant during the course of the tests reported in Table 5. The reaction system became more acid as the reduction progressed. Starting at pH 7, the final pH was between 5 and 6.

TABLE 5

EFFECT OF pH ON DENITRIFICATION

Test No.	Initial pH	Nitrogen Balance, ppm			Denitrification, %
		NO_3^--N	NO_2^--N	NH_3-N	
1. a	6.0	9.8	0	0.5	0
b	6.0	9.5	0	0.4	0
2. a	7.0	3.6	0.6	3.0	28
b	7.0	4.9	0.7	2.2	22
3. a	7.5	2.1	0	3.4	45
b	7.5	2.0	0.9	3.4	37
4. a	8.0	3.5	1.8	3.5	12
b	8.0	3.3	0.9	3.6	22
5. a	8.5	7.0	2.7	0.5	0
b	8.5	3.5	1.1	3.4	20
6. a	9.0	0.8	0.1	4.6	45
b	9.0	2.3	0.4	4.0	33
7. a	11.0	0.1	6.1	1.1	27
b	11.0	0.2	5.7	1.0	31

Fixed Conditions:

Initial NO_3^--N Concentration:	10 ppm
Fe^{++} Concentration:	8%
Catalyst:	Cu^{++}, 5 ppm
Reaction Time:	24 hr
Temperature:	85° F
Atmosphere:	Nitrogen

Starting at 11, the final pH was between 8 and 9. An additional experiment was carried out in which the pH was readjusted manually during the course of duplicate runs in order to hold it near a value of 7. With all other fixed conditions the same as those shown in Table 5, the final nitrogen balances were as follows: NO_3-N, 6.9, 5.7 ppm; NO_2-N, 1.8, 2.3 ppm; NH_3-N, 0.8, 1.4 ppm. Thus, 5% or less denitrification occurred in these runs where pH was held relatively constant.

Effect of Catalysts on Denitrification

The results of a series of tests where catalysts and their concentrations were varied are given in Table 6.

Silver ion (Ag^+) appears to be a much more effective catalyst for reduction than is cupric ion (Cu^{++}) but essentially no denitrification occurred when silver ion was the catalyst.

Silver and cupric ions are the classical homogeneous reduction catalysts (See p. 14 for discussion and references) and their effect is reportedly enhanced by the presence of organic acid anions. In subsequent sections of this report, the use of silver and cupric acetate will be noted, but no effect on denitrification can be attributed to this variation.

Zinc, cadmium, and magnesium ions had no catalytic effect in the reduction reaction in the absence of organic acids. The ability of Zn^{++}, Cd^{++}, and Mg^{++} to catalyze the reduction or denitrification in the presence of an organic acid was not examined because of time limitations.

It is important to remember that this reaction occurs in a heterogeneous system, with precipitated ferrous hydroxide being the reducing agent. The catalysts, Cu^{++} and Ag^+ are, however, the classical homogeneous catalysts, and their mode of action under the present conditions is not readily evident. The heterogeneity of this system may be the source of much of the seemingly erratic behavior in this reaction that is now unexplained. Minor variations in the way $Fe(OH)_2$ is precipitated, the extent to which catalyst ions are absorbed in the precipitate, the manner in which the black ferrous-ferric complex forms from the $Fe(OH)_2$, and a number of other factors associated with the solid state could all play a role.

Effect of Air on Reduction and Denitrification

As noted earlier, the bubbling of air through solutions had confounded our first test results, and data were also presented showing reoxidation of nitrite to nitrate in screening tests (page 19). Analytical studies on this latter effect, which are reported subsequently, showed that nitrite reoxidation would not occur if the solutions remained basic. To further test the effect of air, a reaction was conducted at high pH in an open vessel, with the reaction mixtured stirred mechanically. Under these conditions, 100%

TABLE 6

EFFECT OF CATALYSTS ON DENITRIFICATION

Catalyst		Nitrogen Balance, ppm			Denitrification, %
Type	Conc., ppm	NO_3^--N	NO_2^--N	NH_3-N	
Cu^{++}	1	6.7	2.8	0.8	None
Cu^{++}	5	0.2	5.9	1.0	29
Cu^{++}	10	0.3	5.9	--	--
Ag^{+}	1	0.1	5.9	3.8	(Trace?)
Ag^{+}	5	0.3	8.5	1.1	None
Ag^{+}	10	0.2	5.3	5.1	None

Fixed Conditions: Ag^{+} and Cu^{++} as the sulfate and chloride

NO_3^--N Concentration:	10 ppm
Fe^{++} Concentration:	8X
pH:	11 (initial)
Reaction Time:	24 hr
Temperature:	85° F
Atmosphere:	Nitrogen

Values reported are averages of duplicate runs

reduction was observed, which shows that no NO_3^- is formed by NO_2^- reoxidation under such conditions. However, no denitrification occurred in this test: the final nitrogen balance showed no nitrate; NO_2^--N, 7.8 ppm, and NH_3-N, 2.3 ppm (all fixed conditions, except atmosphere, were the same as Test 7 in Table 5). It is difficult to attribute a failure to denitrify to the presence of air, particularly when reduction has been quantitative. The result may well be confounded by the "occasional unknown cause" mentioned earlier.

Lime for pH Adjustment

In all the work described earlier in this report, sodium hydroxide was used to make initial pH adjustments. Table 7 shows the effect of using lime (CaO) in place of the NaOH.

Lime obviously does not interfere with denitrification unless, as in Test 3, enough lime is added so that the pH remains constant as the lime slowly dissolves. However, some decrease in total reduction may have occurred. Compare Tests 1a and 1b (average 68% reduction) in Table 7 with Test 6 in Table 5. In the latter test, with NaOH, an average of 85% reduction occurred.

Also shown in Table 7 is the effect of increased Fe^{++} level. In Test 2, this drove the reduction largely to NH_3, although some denitrification still occurred.

Effect of Phosphate and Carbonate Ions

The addition of a mixture of phosphate and carbonate ions (as K_2CO_3 and KH_2PO_4) inhibits the reduction reaction. As the duplicate results in Table 8 indicate, this inhibition is caused by the phosphate, probably by deactivating the catalyst.

Phosphate appears to be exceptionally powerful in its ability to inhibit catalysis by Cu^{++}. In additional tests, increases in Cu^{++} concentration to 20 ppm or a change from $CuCl_2$ to cupric acetate ($CuAc_2$), again with an increase to 20 ppm, were unable to overcome the effect. However, two other methods were tested which did prove effective: increasing the iron concentration and substituting Ag^+ for Cu^{++} as the catalyst. Results are shown in Table 9.

Note that in all of the tests above, where $CO_3^=$ alone was present, or where the effect of PO_4^{-3} was overcome by one means or another, there was essentially no denitrification, even though reduction reached the 90%+ level. The carbonate ion buffers these reactions, so that pH remains relatively constant throughout the reaction. Similar results (reduction without denitrification) in the absence of carbonate were noted earlier, when NaOH or lime was added periodically during the course of a reaction so that the pH remained at a high level. Thus, there is an apparent correlation showing that denitrification is suppressed by having a constant pH, although this relationship is partially confounded by the fact that Ag^+, which catalyzed some of the buffered runs, does not appear to induce denitrification even in the absence of carbonate.

TABLE 7

DENITRIFICATION IN THE PRESENCE OF LIME

Test No.	Lime Added ppm	Fe^{++} Level	pH		Nitrogen Balance, ppm			
			Initial	Final	NO_3^--N	NO_2^--N	NH_3-N	"Missing N"
1. a	300	8X	9.0	6.0	3.1	1.6	3.0	2.3
b	300	8X	9.4	6.4	3.3	1.4	3.0	2.3
2.	700	16X	10.2	8.5	0	0.3	7.9	1.8
3.	740	16X	10.5	10.7	4.0	2.4	3.6	None

Fixed Conditions:

NO_3^- Concentration:	10 ppm
Catalyst:	Cu^{++}, 5-10 ppm
Temperature:	85° F
Atmosphere:	Nitrogen
Reaction Time:	24 hr

TABLE 8

EFFECT OF PHOSPHATE AND CARBONATE IONS

pH Adjusted with	pH		PO_4^{-3}-P, ppm	$CO_3^{=}$ ppm	Nitrogen Balance, ppm		
	Initial	Final			NO_3^--N	NO_2^--N	NH_3-N
NaOH	9.5-10	--	10	100	8.2	1.6	0.8
NaOH	9.5-10	--	10	100	7.2	1.4	0.8
NaOH	11	--	10	100	9.3	1.1	--
NaOH	11	--	10	100	8.0	1.4	0.3
Lime	7.0	7.5	10	100	7.8	0	1.3
Lime	7.1	7.5	10	100	8.1	0	1.3
NaOH	10.0	9.9	10	None	9.8	0	0.7
NaOH	9.1	9.7	10	None	8.7	0	1.1
NaOH	10.3	10.2	None	100	1.8	4.3	3.5
NaOH	9.0	8.4	None	100	3.2	1.8	4.4

Fixed Conditions:

NO_3^- Concentration:	10 ppm
Fe^{++} Level:	8X
Temperature:	85° F
Atmosphere:	Nitrogen
Reaction Time:	24 hr
Catalyst:	Cu^{++}, 5 ppm

TABLE

OVERCOMING THE EFFECT OF PHOSPHATE AND CARBONATE

Fe^{++} Level	Catalyst	pH Adjusted with	pH		Nitrogen Balance, ppm		
			Initial	Final	NO_3^--N	NO_2^--N	NH_3-N
16x	Cu^{++}, 5 ppm	NaOH	9.9	10.2	4.7	3.4	2.1
24x	Cu^{++}, 5 ppm	NaOH	9.9	10.3	3.0	3.3	4.0
8x	Ag^+, 5 ppm	Lime	10.5	10.3	1.7	6.8	1.2
8x	Ag^+, 5 ppm (Ag_2SO_4)	Lime	10.5	10.3	2.0	6.8	1.4
8x	Ag^+, 5 ppm	Lime	10.5	9.4	0.9	5.0	3.7
8x	Ag^+, 5 ppm (AgAc)	Lime	10.4	9.4	1.1	5.3	3.3

Fixed Conditions:

NO_3^--N Concentration:	10 ppm
PO_4-P Concentration:	10 ppm
$CO_3^=$ Concentration:	100 ppm
Temperature:	85° F
Atmosphere:	Nitrogen
Reaction Time:	24 hr

There is no immediately evident explanation for the above effect of constant pH. Obviously, pH-related phenomena will have to be investigated in much more detail before applying this reaction in an actual water reclamation process.

ANALYTICAL SUPPORT

Background and Selection of Methods

Nitrate ion, which represents the most highly oxidized phase in the nitrogen cycle, generally occurs in trace quantities in surface water supplies. Since a limit of 45 mg/l nitrate (10 ppm NO_3^--N) has been imposed on drinking waters, a number of analytical chemistry methods are available in the literature to determine NO_3^--N at the ppm level. Methods available in the literature for nitrate ion determination were examined and judged for relative merit with the particular parameters of the nitrate ion reduction effort in mind. For example, for any given set of experiments, analyses were also required for nitrite ion and to complete a material balance, a final analysis for ammonia might be required. All of these were to be determined in the presence of a reducing agent and possibly a deammination agent. Accordingly, methods for nitrite ion and ammonia were also examined. A brief review of the methods considered is given below.

Nitrate and nitrite analyses can be performed according to the method of Fisher, Ibert, and Beckman (Ref. F-6) which utilizes the sulfur-yellow color produced by brucine in sulfuric acid solution. By varying the concentration of sulfuric acid (less than 25% for nitrites, greater than 50% for nitrates) the two can be determined on aliquots as small as 15 ml containing 0-1 micrograms of the anion. A modification of this procedure has been incorporated as a standard method for nitrate in the Standard Methods for the Examination of Water and Wastewater (Ref. F-1). Ferrous and ferric ion have been reported to give slight positive interferences. Interference due to nitrite ion is eliminated by the use of sulfanilic acid. Where nitrate ion alone is desired, another common practice is to destroy the nitrite ion using solid sulfamic acid (NH_2SO_3H). The reaction with sulfamic acid (Ref. F-5) is almost instantaneous and is not interfered with by the species used in the nitrate reduction studies. Nitrite ion may also be determined by the coupling of diazotized sulfanilic acid with 1-naphthylamine hydrochloride at pH 2.0-2.5 with the formation of the reddish purple azo dye (Ref. F-1). The method is sensitive to 0.1 ppm NO_2^--nitrogen in a 10 ml sample. Bastion, et al., (Ref. F-3) reported an ultraviolet spectrophotometric method for the determination of nitrate ion in alkaline earth carbonates. The method is based on the absorption of nitrate ion in the 200-220 millimicron region. The absorption maximum is 200 mμ, but in the systems studied, measurements at 210 were found to give optimum results. Armstrong (Ref. F-2) used a modification of this method to determine nitrate in sea water. The samples are run in 50%

H_2SO_4 and 0.05 M HCl. At these concentrations, both nitrite and nitrate have absorption maxima at 227 mμ. An ultraviolet spectrophotometric method has been recommended in the Standard Methods of Water Examination as useful for screening large numbers of drinking water samples for nitrate ion.

The speed, accuracy, precision, and interferences of each of the above methods were considered in the selection of a candidate procedure for nitrite and nitrate. Of the methods reviewed, the direct measurement of ultraviolet absorbance appeared most desirable with respect to speed and simplicity and was selected for laboratory evaluation. Methods for determination of ammonia were also examined (Ref. F-1, pp 186-194). The method of choice was distillation from a strong base in a micro-Kjeldahl distillation flask, followed by titration with a standard mineral acid. Since urea was a deammination agent under consideration and consequently a source of nitrogen, methods for its determination at the ppm level were reviewed. Two possible methods appeared appropriate (Ref. F-7, F-9). The former is a spectrophotometric procedure using p-dimethylaminobenzaldehyde and the latter is a conversion to ammonia by enzymatic hydrolysis.

Analytical Program

The major part of the analytical program consisted of the evaluation and development of the ultraviolet spectrophotometric method for nitrate and nitrite ion by thoroughly checking out possible interferences from the candidate reducing agents and deammination agents. The ammonia distillation method was examined to determine sensitivity limits and interferences. Subsequent to this, the tentative procedures were applied to the experimental program. From time to time, analytical anomalies arose as a result of changes in the experimental plan (new reducing agent-deammination agent pair, new catalysts, different pH, etc.), or interferences that were not considered at the beginning of the program. These anomalies were investigated and modification or improvements in the methods were made. As the program progressed and ferrous ion became the most frequently used reducing agent, the analysis scheme became routine and the analytical efforts consisted entirely of analysis of samples. A complete description of the ultraviolet spectrophotometric method used is shown in the Appendix at the end of this report.

Development of the Ultraviolet Method

Some of the reagents selected to be screened for the reduction of nitrate and subsequent deammination of nitrite were procured, and solutions of each were prepared. Solutions of potassium nitrate and potassium nitrite were also prepared. Each solution was subjected to ultraviolet spectrophotometric scanning with a Cary 14 Recording Spectrophotometer, covering the region in which nitrate is absorbant. The results of this examination are shown in Table 10.

TABLE 10

UV ABSORBANCE OF NITRATE, NITRITE, AND CANDIDATE AGENTS

Compound	Concentration ppm	Wavelength of Abs. Maximum, mμ	Specific Absorbance, = Optical Density g/l x Cell Thickness
Potassium Nitrate	1 (as N)	205	690
Potassium Nitrite	2 (as N)	210	375
Sucrose	100	< 190	Not applicable
Urea	100	< 190	Not applicable
Formaldehyde	100	< 190	Not applicable
Hydrazine Sulfate	100 (as N_2H_4)	< 190	Not applicable
Sulfamic Acid		< 190	Not applicable
Nitrite + Sulfamic Acid	2 (as N) + large excess	< 190	Only sulfamic acid absorbance seen

Examination of the data in Table 10 reveals that nitrate has an absorption maximum at 205 mμ, and nitrite has a maximum at 210 mμ, in good agreement with ultraviolet spectra recorded elsewhere (Ref. F-2, F-3). It should be noted that although Standard Methods (Ref. F-1) calls for measurements at 220 mμ, this is not an absorption maximum.

The absorbances of the candidate reducing agents at wavelengths below, but near, 190 mμ apparently do not interfere with the nitrate or nitrite absorbance measurements. The solutions were so concentrated relative to the nitrate and nitrite solutions studied that there was some overlap of peak shoulders (or tail) with the 200 mμ region. It is estimated from these studies of individual solutions that at reducing agent concentrations of 50 times that of the nitrate ion, the overlap would introduce an error of about 5% in the nitrate ion determination.

The addition of solid sulfamic acid to a 2 ppm nitrite-N solution, followed by immediate spectrophotometric scan, was found to destroy quantitatively and immediately the nitrite ion. This experiment indicated nitrite ion can be removed easily and quickly. Absorbance measurements before and after nitrite removal will yield values for both ions, by difference calculation.

For the initial phase of the program, four reducing agents were chosen for study:

Ferrous ion (Fe^{++}) as $FeSO_4$
Sulfur dioxide (SO_2)
Filtrasorb 400 carbon
Formaldehyde

The UV spectrophotometric method was further examined for interferences of the above species at stoichiometric and threefold excess. None of these species seemed to interfere with the nitrate determination. Sulfamic acid at threefold concentrations introduced a small error, but this proved easy to correct by use of a reagent blank. Calibration curves were prepared from stock sodium nitrate and sodium nitrite solutions, respectively, and the method was used to analyze the first experimental mixtures. The analytical procedure involved the measurement of the UV absorbance of a diluted portion of the sample, addition of solid sulfamic acid to the diluted solution, and a re-examination of the UV absorbance. Experience showed that measurements at 200 mμ gave the most reproducible results. Since sulfamic acid reacts quantitatively with nitrite ion, the UV absorbance after addition of sulfamic acid was a measure of the nitrate ion and the difference in UV absorbance before and after sulfamic addition was a measure of the nitrite ion.

During the course of the early analyses, deammination evidently was not accomplished in some cases in which it was expected. Study of the problem revealed that incomplete deammination appeared to be restricted to cases

in which the pH was not highly acidic. Data from experiments performed on known sodium nitrite solutions containing sulfamate ion at various concentrations are given in Table 11.

The results shown in Table 11 indicated that deammination did not occur rapidly until the solution was quite acid, and that neither nitrate nor nitrite can be measured by UV absorbance in strongly basic solutions because the hydroxyl ion interferes. Basic sclutions were found not to deamminate completely in 48 hours, but in acid solution the deammination was very rapid.

Indication of the interference by hydroxyl ion prompted pH-absorbance studies. Solutions adjusted to cover the pH range were prepared and their UV spectra were taken on the Cary, Model 14, spectrophotometer. The absorbances at 210 mμ of the solutions are shown in Table 12.

It appears that the hydroxyl ion precludes ultraviolet analysis of basic solutions, and the analytical procedure was altered to include addition of excess acid to the aliquot of sample being diluted for analysis. The work of Bastion (Ref. F-3) showed that perchlorate ion shows no UV absorbance at 230-200 mμ; therefore, acidification of samples was accomplished with perchloric acid. Concentrated perchloric acid is a powerful oxidizing agent, but when diluted to less than 20%, $HClO_4$ has virtually no oxidizing power (Ref. F-8). The amount of perchloric acid necessary to bring the pH of sample solutions below 3 is insufficient to reoxidize nitrite to nitrate during the course of the analysis.

Investigation of sulfite ion interference with UV nitrate analysis was undertaken when test results of solutions containing sodium sulfite showed anomalies between sample and reagent blank when sulfamic acid was added to such solutions. The difficulty was resolved when, in the light of the pH studies described above, it was realized that the addition of sulfamic acid to the sample solution during analysis dramatically changed the pH, and the sample and reagent blank may have been buffered more or less by the sulfite ion. The possibility of sulfamic acid decomposition in basic solution to yield ammonium ion was also considered, but since the high pH solutions could not be analyzed as received, this possibility was not pursued.

The studies indicated that caution must be exercised in interpreting analytical results of some reduction experiments, since deammination was found to be pH-dependent. The effect of pH changes during the analytical procedure which increase the deammination rate were borne in mind, to prevent alteration of nitrite ion content during the analysis.

An examination was made of the air oxidation of standard solutions containing varying concentrations of nitrate and nitrite ion. Using standard handling and transfer procedures, reoxidation of significant amounts of NO_2^- occurred at pH's of 3 or lower when the time of handling exceeded one hour. When analyzing a series of six or more samples, the total analysis time frequently exceeded one hour. At pH's of 7 or above, oxidation did not

TABLE 11

ANALYTICAL STUDY OF SULFAMATE DEAMMINATION

(3 ppm NO_2^--N Level)

Solution No.	Treatment	pH	Absorbance at 210 mμ
1. a	No sulfamic acid	4.0	1.14
b	Increment of sulfamic acid added, lowering pH	3.5	0.82
c	Further increment added	3.0	0.25
d	Further increment added	3.0	0.02
2.	Near stoichiometric amount of sulfamic acid added	2.3	0.05
3.	Sulfamate added, base added	11	OH^- ion interference
4. a	Sulfamate, base added	8.9	1.12
b	Solution acidified	2.7	0.10

TABLE 12

EFFECT OF pH ON UV ABSORPTION

Solution	pH	Absorbance at 210 mμ
NaOH	11	very strong
HCl	5	nil
$HClO_4$	3	nil
NaOH + HCl	3.8	0.03

occur during this time period. Therefore, during analyses of ferrous ion reduction tests, oxidation did not occur during the filtration step as long as the solution was above pH 7. To prevent any reoxidation of NO_2^- at low pH's, the procedure was modified so that each sample was scanned in the appropriate UV range immediately after the acidification step.

The procedure described in the Appendix was used to carry out a series of tests on standard nitrate-nitrite mixtures to establish error limits. For samples containing 50 ppm total N, the limits of the procedure were found to be less than 1 ppm for NO_3^-, and less than 2 ppm for NO_2^- when a large amount of NO_3^- is also present.

Ammonia Distillation Method

Analysis for ammonia was examined to ascertain the lower limits of detection by the distillation method, and possible interferences from nitrogeneous reducing and deammination agents. Some literature information on the stability of the sulfamate ion was obtained (Ref. F-4); however, analysis of known standards containing ferrous ion and sulfamic acid was considered necessary. The distillation method, deemed most reliable for the purpose of the reduction study, involved the addition of an aliquot of the sample and a volume of sodium hydroxide to a small still. Ammonia in the sample is steam distilled, caught in a boric acid solution, and titrated with dilute standard acid solution. The examination of nitrate and reducing agent solutions was performed with 25 ml aliquots of each solution studied. The results are shown in Table 13.

The data of Table 13 show that recovery of ammonia from dilute solutions of ammonium ion is sufficiently quantitative to monitor formation of ammonia from nitrate reduction at the levels of interest in this effort. However, the recovery of ammonia from solutions prepared with ferrous sulfate and nitrate, and with sulfamic acid, are potential sources of error. The sulfamic acid contribution of ammonia may be the result of slow decomposition of the reagent. The ferrous sulfate or nitrate alone yielded no ammonia, but the combination yielded ammonia, indicating that reduction of nitrate to ammonia occurred to some extent under the conditions of the distillation. The error, however, was only about 1 ppm at the 50 ppm nitrate nitrogen level and the method was used without further modification.

TABLE 13

AMMONIA DETERMINATIONS ON SYNTHETIC NITRATE REDUCTION SAMPLES

(25 ml Aliquots in All Cases)

Solution	Ammonia Nitrogen	
	ppm Added	ppm Recovered
Ammonium salt	1	0.96
Ammonium salt	10	9.9
50 ppm NO_3^--N (plus 3 x stoichiometric amount of $FeSO_4 \cdot 7H_2O$ (150 mg) plus 3 x stoichiometric amount of NH_2SO_3H (26 mg)	0	1.2
50 ppm NO_3^--N	0	0
150 mg $FeSO_4 \cdot 7H_2O$	0	0
26 mg NH_2SO_3H	0	0.2
50 ppm NO_3^--N plus 150 mg $FeSO_4 \cdot 7H_2O$	0	0.9
50 ppm NO_3^--N plus 200 mg $FeSO_4 \cdot 7H_2O$	0	1.9

EXPERIMENTAL DETAILS

APPARATUS

Reactions were conducted in 200 ml volumetric flasks, each containing a mechanical stirrer and a tube inserted into the neck to provide the appropriate gaseous atmosphere. (During the first few reactions, the gas tubes were inserted into the liquid, and the gas bubbled through, but this process did not effectively stir suspended solids, and was abandoned.) The reactors were immersed in a thermostatted water bath during the reaction period. Adjustments and changes in pH were monitored with a Beckman pH meter (Model G).

REAGENTS

Reagents and their sources are listed below:

Water, H_2O	- From a laboratory demineralizer
Potassium Nitrate, KNO_3	- J. T. Baker Chem. Co.
Sodium Nitrite, $NaNO_2$	- J. T. Baker Chem. Co.
Sodium Hydroxide, NaOH	- Mallinckrodt Chem. Works
Ferrous Sulfate, $FeSO_4 \cdot 7H_2O$	- J. T. Baker Chem. Co.
Carbon, C	- Calgon Corporation's Filtrasorb 400
Sulfur Dioxide, SO_2	- The Matheson Co.
Formaldehyde, CH_2O	- 36.6% Formalin, J. T. Baker Chem. Co.
Glucose, $C_6H_{12}O_6$	- Eastman Organic Chem. Co.
Iron Powder, Fe	- Mallinckrodt
Hydrazine, N_2H_4	- Eastman
Hydrazine Sulfate, $N_2H_6SO_4$	- Fisher Scientific Co.
Carbon Monoxide, CO	- The Matheson Co.
Sulfamic Acid, NH_2SO_3H	- Eastman
Cupric Chloride, $CuCl_2$	- Mallinckrodt
Silver Sulfate, Ag_2SO_4	- J. T. Baker
Cupric Acetate, $Cu(C_2H_3O_2)_2$	- J. T. Baker
Silver Acetate, $AgC_2H_3O_2$	- Mallinckrodt

Ferric Chloride, $FeCl_3 \cdot 6H_2O$	- J. T. Baker
Ammonium Vanadate, NH_4VO_3	- Harshaw Scientific
Vanadium Pentoxide, V_2O_5	- J. T. Baker
Lime, CaO	- J. T. Baker
Potassium Carbonate, K_2CO_3	- J. T. Baker
Potassium Phosphate, Monobasic, KH_2PO_4	- General Chem. Division, Allied Chem.

PROCEDURE

A typical experiment with $FeSO_4$ as the reducing agent is described below. Note that a blank (demineralized water with no NO_3^-) was treated in the same manner as described for the sample.

Test samples were prepared by adding standard nitrate solutions (2 mg NO_3^--N/ml) by means of a small burette to water contained in 200 ml volumetric flasks. The volume of the water was initially just short of the desired 200 ml. After the addition of the various reagents, the volume was adjusted to the 200 ml mark. Ferrous ion was added to the nitrate solution in the form of the solid $FeSO_4 \cdot 7H_2O$ (carefully weighed on the analytical balance). The catalyst solution (ie., 1 mg Cu^{++}/ml) was then added by means of a pipette. After thorough mixing, the pH of the solution was adjusted to the desired level by adding a few drops of a sodium hydroxide solution (6M). The pH of the blank was first adjusted in order to establish the volume of base necessary to reach the desired pH. Addition of the same volume of base to the test samples, made further adjustments unnecessary. Next, the flasks were placed in a constant temperature bath (85° F) and stirred mechanically under a blanket of nitrogen gas. At the end of the reaction period, samples were withdrawn for pH determination, nitrate-nitrite analyses and ammonia analysis.

Deammination experiments involved urea and sulfamic acid. These were usually added just prior to the pH adjustment. Urea was added as the solid. Sulfamic acid was added as the basic salt (neutralized with NaOH, pH 8) in water solution (10 mg N/ml).

For the experiments where phosphate, carbonate, and lime were used the order of addition consisted of: adding phosphate solution (2 mg P/ml) to the nitrate solution, then adding the carbonate solution (20 mg $CO_3^=$/ml), adding weighed amounts of lime (with thorough shaking), then adding $FeSO_4$, and adding the catalyst solution at the very end.

TEST RESULTS

With the exception of the reducing agent screening series, details of all reactions have been tabulated in the DISCUSSION AND RESULTS section of this report. The screening test results are given here in Table 14.

TABLE 14

SCREENING OF REDUCING AGENTS

Fixed Conditions:

NO_3^- Concentration:	50 ppm
Temperature:	85° F
Atmosphere:	Nitrogen
Reaction Time:	48 hr
Reducing Agent Concentration:	3x } Denotes 3 moles of agent per
Deammination Agent Concentration:	3x } mole of NO_3^-

(Occasional variation in conditions noted in test)

Reducing Agent	Deammination Agent (when added)	Catalyst (concentration, ppm)	pH	NO_3^--N, ppm	
				After 24 hours	After 48 hours
SO_2	$NaSO_3NH_2$	Fe^{+++}(2.5)	9	49.7	48.4
SO_2	$NaSO_3NH_2$ (24 hr)	Cu^{++} (2.5)	9	51.8	49.9
SO_2	HSO_3NH_2 (start)	Fe^{+++}(2.5)	6	50.7	50.8
SO_2	HSO_3NH_2 (start)	Cu^{++}(2.5)	6	50.2	50.7
Carbon					
C	HSO_3NH_2 (24 hr)	Fe^{+++}(5)	6	50.8	51.1
C	HSO_3NH_2 (24 hr)	Cu^{++}(5)	6	51.4	52.4
C	HSO_3NH_2 (Start)	Fe^{+++}(5)	6	49.2	50.3
C	HSO_3NH_2 (Start)	Cu^{++}(5)	6	50.9	53.4 (?)

TABLE 14 (CONT'D)

Reducing Agent	Deammination Agent (when added)	Catalyst (concentration, ppm)	pH	NO_3^--N, ppm	
				After 24 hours	After 48 hours
Formaldehyde					
CH_2O	HSO_3NH_2 (start)	Fe^{+++}(2.5)	6	49.8	49.9
CH_2O	HSO_3NH_2 (start)	Cu^{++}(2.5)	6	50.2	49.7
CH_2O	HSO_3NH_2 (24 hr)	Fe^{+++}(5)	6	50.2	50.7
CH_2O	HSO_3NH_2 (24 hr)	Cu^{++}(5)	6	50.9	51.2
Carbon Monoxide					
CO	None	Cu^{++}(5)	6	49.8	--
CO	$CO(NH_2)_2$	Cu^{++}(5)	6	51.7	--
Glucose					
$C_6H_{12}O_6$	$CO(NH_2)_2$ (24 hr)	Fe^{+++}(5)	6	49.5	49.0
$C_6H_{12}O_6$	$CO(NH_2)_2$ (24 hr)	Cu^{++}(5)	6	49.4	49.1
$C_6H_{12}C_6$	$CO(NH_2)_2$ (start)	V^{+5}(5)	6	50.1	48.5 (NO_2^--N, 2.8)
$C_6H_{12}O_6$	None	V^{+5}(10)	4	47.6 (NO_2^--N, 2.4)	48.4 (NO_2^--N, 1.4)
$C_6H_{12}O_6$	None	V^{+5}(10)	4	48.9 (NO_2^--N, 3.5)	49.8 (NO_2^--N, 2.6)

TABLE 14 (CONT'D)

Reducing Agent	Deammination Agent (when added)	Catalyst (concentration, ppm)	pH	NO_3^--N, ppm	
				After 24 hours	After 48 hours
Hydrazine					
N_2H_4	$CO(NH_2)_2$ (24 hr)	Fe^{+++}(0.7)	11	50.4	41.5
N_2H_4	$CO(NH_2)_2$ (24 hr)	Cu^{++}(0.7)	11	46.2	43.6
N_2H_4	$CO(NH_2)_2$ (start)	Cu^{++}(0.5)	11	48.8	30.4
Hydrazine Sulfate					
$N_2H_6SO_4$ (3.75X)	None	Cu^{++}(0.25)	11	48.2 (NO_2^--N, 3.4)	44.5 (NO_2^--N, 0.4)
$N_2H_6SO_4$ (3.75X)	None	Cu^{++}(0.25)	11	43.9 (NO_2^--N, 8.6)	40.4 (NO_2^--N, 0)
$N_2H_6SO_4$ (3.75X)	None	Cu^{++}(1)	11	48.6 (NO_2^--N, 3.2)	41.8 (NO_2^--N, 5.2)
$N_2H_6SO_4$ (3.75X)	None	Cu^{++}(1)	11	48.0 (NO_2^--N, 4.4)	41.3 (NO_2^--N, 5.4)
Iron Powder					
Fe	HSO_3NH_2 (24 hr)	Fe^{++}(2.5)	6	53.6(?)	59.5(?)
Fe	HSO_3NH_2 (24 hr)	Cu^{++}(2.5)	6	45.3	43.5
Fe	$CO(NH_2)_2$ (start)	Cu^{++}(2.5)	6	49.5	48.9
Fe (4.5X)	None	Cu^{++}(10)	6	40.4 (NO_2^--N, 6.8)	27.3 (NO_2^--N, 4.8)
Fe (4.5X)	None	Cu^{++}(10)	6	29.9 (NO_2^--N, 14.8)	27.4 (NO_2^--N, 10.3)

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APPENDIX

ANALYTICAL PROCEDURE FOR THE SIMULTANEOUS DETERMINATION OF NITRATE AND NITRITE IONS

Nitrate and nitrite can be simultaneously determined from a solution containing insoluble matter, either with or without a deammination agent present, using ultraviolet spectroscopic methods.

Apparatus and Reagents

Cary 14 recording spectrophotometer with a set of matched 1 cm silica cells.

Standard volumetric glassware.

70-72% Perchloric acid; Baker "analyzed" grade.

Sulfamic acid; 99+% Eastman white label.

Sodium nitrate; Baker "analyzed" grade.

Sodium nitrite; Baker "analyzed" grade.

Sodium nitrate stock solution; prepare by dissolving 0.6071 gm of sodium nitrate in 1 liter of distilled water to form a stock solution of 100 ppm nitrogen.

Sodium nitrite stock solution; prepare by dissolving 0.4929 gm of sodium nitrite in 1 liter of distilled water to form a stock solution of 100 ppm nitrogen.

Preparation of Calibration Curves

Make up a set of six standard solutions of mixtures of sodium nitrate and sodium nitrite in distilled water such that each solution contains a total of 50 ppm nitrogen. Also make up a blank. Prepare these solutions by diluting the following volumes of stock nitrate and nitrite solutions to 50 ml:

1.	0.00 ml NO_3^-	25.00 ml NO_2^-
2.	5.00 ml NO_3^-	20.00 ml NO_2^-
3.	10.00 ml NO_3^-	15.00 ml NO_2^-

4.	20.00 ml NO_3^-	10.00 ml NO_2^-
5.	20.00 ml NO_3^-	5.00 ml NO_2^-
6.	25.00 ml NO_3^-	0.00 ml NO_2^-

The blank should contain only distilled water. The concentrations of the above solutions are as follows:

1.	0 ppm NO_3^--N	50 ppm NO_2^--N
2.	10 ppm NO_3^--N	40 ppm NO_2^--N
3.	20 ppm NO_3^--N	30 ppm NO_2^--N
4.	30 ppm NO_3^--N	20 ppm NO_2^--N
5.	40 ppm NO_3^--N	10 ppm NO_2^--N
6.	50 ppm NO_3^--N	0 ppm NO_2^--N

The blank is zero in both.

Pipet 4 ml of each standard into clean 100 ml volumetric flasks and 80-90 ml of distilled water. Do not dilute to the mark.

Check the matched silica cells for cleanliness by scanning from 250-195 millimicrons with distilled water in both cells. If the baseline varies more than 0.005 absorbance units, reclean the cells.

To the first solution, add 4 drops of 70-72% perchloric acid and dilute to the mark. This should lower the pH to 2. Immediately scan from 250-195 millimicrons using distilled water as a reference. Read at 200 millimicrons and call this absorbance A. Add a threefold excess (approximately 4 mg) of solid sulfamic acid to the flask. Mix well and scan this solution from 250-195 millimicrons. Read this at 200 millimicrons and call this absorbance B. Repeat for each standard solution and the blank.

Since sulfamic acid has a slight absorbance at 200 millimicrons (1/500 that of NO_3^-) care must be taken not to add too large an excess and to add a fairly constant amount to both sample and blank. Correct the absorbances A and B by subtracting the appropriate blanks.

Absorbance B is proportional to the NO_3^- concentration. Plot ppm nitrate nitrogen vs absorbance B. Call this plot curve 1.

Absorbance A minus absorbance B is proportional to NO_2^- concentration. Plot ppm nitrite nitrogen vs absorbance A minus absorbance B. Call this plot curve 2.

Procedure with Deammination Agent Absent

If the sample has insoluble matter, filter about 15 ml through Whatman 42 filter paper.

Follow the procedure outlined in the calibration curve discussion with the following variations. If the sample started out at 50 ppm NO_3^--N, dilute 5 ml to 25 ml. A reagent blank is essential and must be treated exactly like a sample. The reagent blank should include the reducing agent, catalysts, be the identical pH of the sample, and treated under the same temperature and time conditions of the sample.

Calculations

Read all values at 200 millimicrons. To get the true value for each absorbance, the appropriate blank must be subtracted before any calculations.

Absorbance B is absorbance due to NO_3^--N. Calculate ppm nitrate-N from Curve 1.

Absorbance A minus absorbance B is absorbance due to nitrite-N. Calculate ppm nitrite-N from Curve 2.

Multiply by the dilution factor to obtain the original nitrate and nitrite concentrations.

Interferences

Most anions interfere somewhat at 200 millimicrons. However, they are much weaker absorbers than either NO_3^- or NO_2^-. If the reagent blank has been carefully made up and handled, these interferences can easily be subtracted out giving rise to very little error.

ALTERNATE PROCEDURE FOR SOLUTIONS CONTAINING A DEAMMINATION AGENT

Calibration

A third curve must be prepared for nitrite ion at neutral pH's.

Scan a series of nitrite solutions containing 0-2 ppm nitrite nitrogen in distilled water, from 250-195 millimicrons. Read the absorbance values at 200 millimicrons. Plot the absorbance at 200 millimicrons vs ppm NO_2^--N. Call this Curve 3.

Procedure

Two aliquots of each solution must be taken. The first aliquot is adjusted to pH between 7 and 9, diluted to the mark, and scanned "as is"

from 250-195 millimicrons. Read the absorbance at 200 millimicrons and call this value absorbance C. Treat the second aliquot exactly as before to obtain absorbances A and B. Absorbances A and B are equal if the deammination agent present is there in sufficient quantity to deamminate the solution as the pH is lowered to 2.

Calculations

Absorbance B is due to the absorbance of NO_3^- ion. Read from Curve 1.

Absorbance C minus absorbance B is due to the absorbance of NO_2^- ion. Read from Curve 3.

Calculate the results in the same manner as shown in the preceding section.